An Octanuclear Cd–Sn-(μ_4-O)$_2$ Complex with Bridging Acetate and Neopentoxide Groups: [$Cd_4Sn_4(\mu_4\text{-}O)_2(O_2CMe)_{10}(OCH_2Bu^t)_{10}$]

Clive Chandler, Gary D. Fallon, and Bruce O. West*

Department of Chemistry, Monash University, Clayton, Victoria, Australia, 3168

Cadmium acetate and tin(IV) tetraneopentoxide react in tetrahydrofuran to form [$Cd_4Sn_4(\mu_4\text{-}O)_2(O_2CMe)_{10}(OCH_2Bu^t)_{10}$] containing an 8-membered, Cd_4O_4 planar ring with cadmium ions bridged by acetates and further linked in pairs by μ_4-oxo, acetate, and neopentoxide bridges to two tin(IV) atoms which in turn are bridged by neopentoxide and acetate groups.

Solutions of metal alkoxides, often with added acetate, acetylacetone (Hacac), or other chelating ligands are favoured precursor materials for the formation of homonuclear and heteronuclear metal oxides by the hydrolytic 'sol–gel' process.[1—3] Alkoxide groups particularly but also the other types of ligands are capable of bridging metal ions and hence can support the formation of polynuclear complexes in solution. Such complex formation is of advantage to the 'sol–gel' process since a framework of M–O bonds is thus formed. If this framework is maintained through the hydrolytic phase of the process the stoicheiometry and structure of the final oxide system formed after pyrolytic olation may be controlled. Such solution complexation may be of particular importance in processes designed to yield heteronuclear oxide systems, since inhomogeneity in the final oxide system due to differential deposition of the various constituent metal hydroxides may be avoided. The creation of oxo bridging in such complexes by olation or other routes in solution prior to the final pyrolytic conversion of the 'gel' to the oxide would also be an advantage.

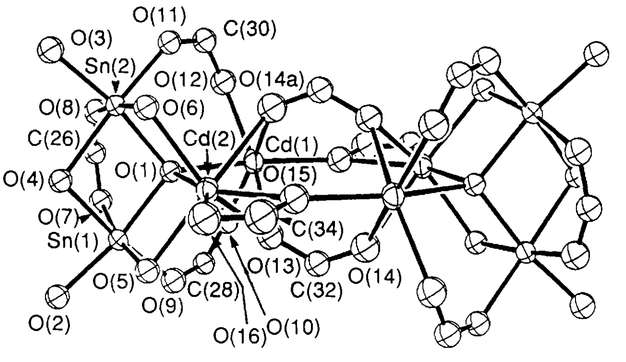

Figure 1. Molecular structure of [$Cd_4Sn_4(\mu_4\text{-}O)_2(O_2CMe)_{10}(OCH_2\text{-}Bu^t)_{10}$]. (The CH_2Bu^t segment of neopentoxide and Me of acetate are omitted for clarity.) Selected interatomic distances (Å) and angles (°): Sn(1)–O(4), 2.104(16); Sn(2)–O(3), 1.965(19); Sn(2)–O(6), 2.034(15); Sn(2)–O(8), 2.185(17); Sn(1)–O(9), 2.064(18); Cd(2)–O(6), 2.284(17); Cd(1)–O(12), 2.301(20); Cd(2)–O(15), 2.346(18); Cd(2)–O(16), 2.310(18); Cd(1)–O(15A), 2.256(20); Sn(1)–O(1)–Sn(2), 103.4(7); Sn(1)–O(4)–Sn(2), 97.7(7); Sn(2)–O(1)–Cd(1), 124.3(8); Sn(2)–O(1)–Cd(2), 101.8(6); Sn(2)–O(6)–Cd(2), 103.9(7); Cd(1)–O(1)–Cd(2), 124.5(7); Cd(1)–O(13)–Cd(2), 90.3(7); Cd(2)–O(15)–Cd(1A), 128.7(8); O(1)–Sn(1)–O(7), 87.5(6); O(1)–Cd(1)–O(15A), 166.8(6); O(1)–Cd(2)–O(15), 148.9(6); O(5)–Cd(2)–O(6), 106.4(6); O(15)–Cd(2)–O(16), 54.7(7); O(15)–Cd(2)–O(13), 82.4(6).

For polynuclear alkoxo-bridged systems have yet been structurally characterized.[4] Important recent studies have included [$Ti_6(\mu\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}OBu^n)_2(OBu^n)_6(O_2CMe)_8$], a component[5] of solutions used in TiO_2 production, [$\{Y(OC_2H_4OMe)_3\}_{10}$], a compound used in preparing $YBa_2Cu_3O_{7-x}$ superconducting species, while [$Ba_2Cu_2(OCH_2CH_2OMe)_4(acac)_4$] has been isolated from solutions used to prepare films of superconducting oxides.[7]

We have been examining the interactions between cadmium alkanoates and tin(IV) alkoxides in various solvents and attempting to isolate and structurally characterise the complexes formed in solution. Such mixtures have been recommended for use in the preparation of cadmium stannate (Cd_2SnO_4) by the sol-gel process.[8] There is considerable interest in this material because of its optical and electrical properties particularly when applied as a thin film.[9]

The interaction of anhydrous cadmium acetate[10]† with the three tin(IV) alkoxides, $Sn(OPr^i)_4$, $Sn(OBu^t)_4$, and $Sn(OCH_2Bu^t)_4$ has been examined, each alkoxide bearing groups of different stereochemical significance.

The acetate is insoluble in toluene but dissolves readily on heating in the presence of a molar equivalent of $Sn(OPr^i)_4$. This alkoxide is associated in benzene solution[11] so that alkoxy bridging between Sn ions can clearly occur. The hot solution rapidly deposits a white, sparingly soluble product which has the microanalytical composition $Cd(O_2CMe)_2{\cdot}Sn(OPr^i)_4$. The compound will redissolve in toluene in the presence of a further mole of $Cd(O_2CMe)_2$ suggesting the formation of a 2Cd–Sn species but a homogeneous product has not been

---

† $Cd(O_2CMe)_2.2H_2O$ was heated at 100 °C *in vacuo* (10^{-4} Torr) for 2 h. The IR spectrum of the product showed no evidence for OH stretching vibrations. All experiments subsequently were carried out under anhydrous conditions using standard vacuum-line, dry-box, and Schlenk techniques.

recovered from the mixture. $Sn(OBu^t)_4$, which is not associated in organic solvents,[11] indicating that such bulky groups can prevent alkoxide bridging, does not react with cadmium acetate in toluene supporting the hypothesis that Cd–Sn bridging by an alkoxide group is a necessary condition of reaction between the metal compounds.

However the neopentoxide $Sn(OCH_2Bu^t)_4$, [Sn(ONep)$_4$], where the bulky Bu^t group is further removed from oxygen, reacts readily with an equimolar amount of cadmium acetate in tetrahydrofuran solution yielding a moderately soluble compound having a microanalytical composition corresponding to $Cd_2Sn_2(O)(ONep)_5(O_2CMe)_5$. A suitable crystal has been submitted to an *X*-ray diffraction study‡ disclosing that the compound is a centrosymmetric octanuclear species containing four Cd and four Sn atoms in the molecule (Figure 1).

The molecular unit includes a planar 8-membered ring containing four Cd atoms linked in pairs by single oxygen atoms of two acetate ions each of which is also chelated to one of the Cd atoms being bridged. The ring is completed by two oxo groups each linking two cadmium atoms on opposite sides of the ring. Pairs of Sn atoms are in turn bonded to the oxo ions which are thus four-co-ordinate.

The two groups of Sn_2O atoms lie in planes parallel to each other, virtually at right angles (91°) to the Cd_4O_4 plane. The 'Sn_2O' planes intersect the Cd_4O_4 plane at angles of 18.9° to the [μ_4-O(1)]–[μ_4-O(1A)] axis. The $Sn_2(\mu_4\text{-}O)Cd_2$ units depart significantly from regular tetrahedral stereochemistry as observed in $[Zn_4(\mu_4\text{-}O)(O_2CMe)_6]$.[12]

Each pair of Sn atoms is bridged by both an acetate and a neopentoxide group and each Sn atom is further linked to one neighbouring Cd by an acetate bridge and to the other 'near neighbour' Cd by a neopentoxide bridge. The structure of the molecule is completed by single terminal neopentoxide groups at each Sn and two acetate groups lying above and below the Cd_4O_4 ring in 'coat hanger' fashion along the [μ_4-O(1)]–[μ_4-O(1A)] axis. Each acetate O is equidistant from a pair of Cd atoms and within bonding distance to each.

Two Cd atoms in the molecule are thus seven-co-ordinate and two six-co-ordinate. The Sn–O (acetate and alkoxide) and Cd–O (acetate) distances are comparable with other values previously reported for Sn alkoxide[13] and acetate[14,15] and Cd acetate species.[16,17]

IR spectral bands at 1574 and 1418 cm^{-1} would appear to be due to the antisymmetric (ν_8) and symmetric (ν_3) stretching frequencies of CO groups in bridging acetates, the difference ($\nu_8 - \nu_3 = 156\ cm^{-1}$) being of the same order of magnitude as observed for $[Zn_4O(O_2CMe)_6]$ and $[Be_4O(O_2CMe)_6]$.[17] The ^1H NMR spectrum of the complex, although showing multiplets centred around δ 3.31 (CH_2), 2.07 (O_2CMe), and 0.91 (Bu^t), is not sufficiently resolved at 200 MHz to allow terminal or bridging alkoxide or acetates to be distinguished.

The constitution of the complex raises two linked questions: (i) the origin of the oxo groups and (ii) the decreased number of alkoxy groups relative to the number of Sn^{IV} atoms present compared to the increased number of acetate ions relative to Cd, their initial source. The mode of formation of the oxo groups is not clear at this stage. Although considerable care was exercised in working with this system under anhydrous conditions it is conceivable that the presence of adventitious moisture may have contributed to the formation of the oxo groups by hydrolysis of alkoxide groups and subsequent olation. However unexpected oxo group formation has also been noted in the preparation of $In_5(\mu_5\text{-}O)(OPr^i)_{13}$[18] and $Y_5(\mu_5\text{-}O)(OPr^i)_{13}$[19] and its possible formation by elimination of an ether between two alkoxide groups was raised by the latter authors. Neither hydrolysis nor ether elimination alone can account for the 'shortage' of alkoxide groups relative to the number of Sn ions in the present complex. This fact plus the 'excess' of acetate ions present relative to Cd indicates that the complex isolated was not the sole species formed in solution.

Work is continuing on the behaviour of this and other related complexes in solution with the objective of defining any relationship between chemical constitution and the utility of such compounds in the sol–gel process.

We thank Monash University for support *via* a tutorship (to C. C.) and the Australian Research Council for a grant (to B. O. W.).

Received, 21st March 1990; Com. 0/01244K

References

1 L. G. Hubert-Pfalzgraf, *New J. Chem.*, 1987, **11**, 663.

2 H. Dislich, in 'Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Speciality Shapes,' ed. L. C. Klein, Noyes Publications, New Jersey, 1988, ch. 4.

3 D. C. Bradley, *Chem. Rev.*, 1989, **89**, 1317.

4 R. C. Mehrotra, D. C. Bradley, and D. P. Gaur, 'Metal Alkoxides,' Academic Press, 1978: R. C. Mehrotra, *Adv. Inorg. Radiochem.*, 1983, **26**, 269.

5 S. Doeff, Y. Dromzee, F. Taulelle, and C. Sanchez, *Inorg. Chem.*, 1989, **28**, 4439.

6 O. Poncelet, L. G. Hubert-Pfalzgraf, J.-C. Daran, and R. Astier, *J. Chem. Soc., Chem. Commun.*, 1989, 1846.

7 N. N. Sauer, E. Garcia, K. V. Salazar, R. R. Ryan, and J. A. Martin, *J. Am. Chem. Soc.*, 1990, **112**, 1524.

8 H. Dislich, P. Hinz, and G. Wolf, US Pat. 4229491, Dec. 13, 1977; assigned to Jenaer Glaswerk Schott and Gen., Mainz, FRG.

9 C. M. Lambert, *Solar Energy Mat.*, 1981, **6**, 1.

10 M. A. Bernard and F. Busnot, *Bull. Chim. Soc. Fr.*, 1967, 4649.

11 J. C. Maire, *Ann. Chim. (Paris)*, 1961, 969.

12 L. Hiltunen, M. Lesbela, M. Mäkelä, and L. Niinistö, *Acta Chem. Scand., Sect. A*, 1987, **41**, 548.

13 C. D. Chandler, G. D. Fallon, A. J. Koplick, and B. O. West, *Aust. J. Chem.*, 1987, **40**, 1427.

14 N. W. Alcock and V. L. Tracy, *Acta Crystallogr., Sect. B*, 1979, **35**, 80.

15 N. W. Alcock and V. L. Tracy, *J. Chem. Soc., Dalton Trans.*, 1976, 2246.

16 W. Harrison and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1972, 956.

17 N. W. Alcock, V. M. Tracy, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1976, 2243.

18 D. C. Bradley, H. Chudrzynska, D. M. Frigo, M. B. Hursthouse, and M. A. Mazid, *J. Chem. Soc., Chem. Commun.*, 1988, 1258.

19 O. Poncelet, W. J. Sartain, L. G. Hubert-Pfalzgraf, K. Foltung, and K. G. Caulton, *Inorg. Chem.*, 1989, **28**, 263.

---

‡ *Crystal data* for $Cd_4Sn_4C_{70}H_{140}O_{32}$: $M = 2418$, monoclinic, space group *C2/c*, $a = 25.316(15)$, $b = 15.076(7)$, $c = 28.221(10)$ Å, $\beta = 98.16(4)°$, $U = 10662(9)$ Å^3, $D_c = 1.51$ g cm^{-3}, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 17.7$ cm^{-1}, $F(000) = 4832$, $T = 293(1)$ K. Nicolet R3m/V diffractometer, graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å); 9356 unique data collected ($4.0 < 2\theta < 50°$), 2924 with $F \geqslant 6\sigma(F)$. Three standard reflections monitored every 197 reflections showed a 17% drop in intensity over the data collection period. Intensity data were corrected for Lorentz and polarization effects and allowance made for the decay. A numerical absorption correction was applied, (transmission factors: maximum 0.987, minimum 0.964). Anomalous dispersion corrections were applied to atomic scattering factors for neutral atoms. Structure solved by Patterson and Fourier methods. Full-matrix least-squares refinement (SHELXTL PLUS Revision 3.4) employing anisotropic thermal parameters for Cd and Sn and isotropic thermal parameters for all other atoms (single fixed parameter for hydrogen positioned in geometrically idealized positions: C–H 0.96 Å), converged at $R = 0.070$ and $R_w = 0.089$. Largest peak in the difference Fourier synthesis was 1.25 e Å^{-3}. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.